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Attention: 8(d) HEALTH and SAFETY REPORTING RULE (REPORTING)
May 1, 1987

Dear Sir or Madam:

As described at 40 C.F.R. 716.20(a) (10), the International Isocyanate Institute (III) submits the enclosed studies on behalf of its members to satisfy member reporting requirements under Section 8(d) of the Toxic Substances Control Act. These studies are on chemicals added to the 8(d) list on May 1, 1987. The studies are indexed by CAS numbers with chemical name, III identification number and title provided.

Attachment #1 is an indexed list of completed studies.

Attachment #2 is a compilation of the reports from the completed studies.

Attachment #3 is an indexed list of studies that are currently in progress.

Please refer to the III identification number in any communication regarding the report.

If the Agency needs further information, please do not hesitate to contact me.

Very truly yours,

R. K. Rigger
Managing Director

RKR/c
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REPORT ON LIQUID WASTE AFTER TDI/MDI DECONTAMINATION

PREPARED FOR

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* The work described in this Report was supported financially by III. It has not been evaluated or interpreted by III's Safety Committee and accordingly III makes no representations regarding conclusions if any to be drawn from this work. Subject to the foregoing this Report is only available for internal circulation within Member Companies of III.

#1321 - 38-6

Report to International Isocyanate Institute
Project EE 25, Liquid waste after TDI/MDI decontamination

The nature of Liquid waste should be investigated, remaining after decontamination of empty TDI- or MDI-barrels with aqueous solutions, according to Project Proposal of March 198o.

Isocyanate residue in empty barrels

The residue after emptiing 2oo l steel drums was determined by the following procedure: 1o kg MDI or TDI were filled into the barrel, the closed barrel rolled 4o m; a cock was connected to the barrel which was tilted to an angle of 45° and emptied until only droplets came out. The remaining residue was determined by weight difference. As a mean value of 9 measurements we found with raw MDI (Lupranat M 2o) 344 g residue, with TDI (Lupranat T 8o) 83 g residue per barrel.

Decontamination with aqueous solutions, semiquantitative screening test

1 l tin cans were filld with TDI respective MDI which was then poured out (1o seconds). Residues between 3,1 and 3,5 g TDI respectively 34,8 - 36,1 g MDI remained in the tin can. The can was then refilled with 1 l of the following decontaminants (these decontaminants were scheduled in the I.I.I. research project proposal of March 198o):

1. 9o % water, 8 % conc. ammonia water, 2 % detergent (Lutenso

2. 5o % ethanol, 5 % conc. ammonia water, 45 % water

3. 5 % sodium carbonate, 95 % water

4. 7,5 % conc. ammonia water, o,5 % detergent (Lutensol AP 1o), 92 % water

5. drinking water.

After 18 days at room temperature the Liquid was decanted and analysed. The solid residue was not collected quantitatively in this preliminary tests. Table 1 shows the pH-value and the nitrogen content of the aqueous phase, which was decanted from the solid. In case of decontaminant I theoretically 15,3 g/l NH_3 (or 1,26 % N) should be found in the decanted solution from MDI or 19,7 g/l NH_3 (or 1,62 % N) from TDI (N calculated from NH_3 af sub traction of isocyanate). The decontaminants 2 and 4 contain little smaller amount of ammonia. Due to evaporation of ammonia the N-values cited in table 1 are far lower, unfortunately the analysis was performed after 18 days.

With water or sodium carbonate solution as decontaminant less than o.o5 % N were found, indicating at least in case of MDI that the greatest part of MDI-reaction product was not dissolved in the water phase but was precipitated.

Table 1 pH and nitrogen content of alkaline decontaminants

Decontaminated Isocyanate	Decontamination Agent	pH-value	Nitrogen % (Kjeldahl)
Crude MDI	8 % NH_3, 2 % Lutensol AP 1o	8,8	o,16
	5o % C_2H_5OH, 5 % NH_3	9,o	o,13
	5 % Na_2CO_3	1o,1	<o,o5
	7.5 % NH_3, o,5 % Lutensol AP 1o	9,2	o,24
	water	5,5	<o,o5
TDI	8 % NH_3, 2 % Lutensol AP 1o	9,3	o,16
	5o % C_2H_5OH, 5 % NH_3	9,o	o,14
	5 % Na_2CO_3	1o,6	<o,o5
	7,5 % NH_3, o,5 % Lutensol AP 1o	8,5	o,o9
	water	7,4	<o,o5

Sodium carbonate solution is not an useful decontaminant. After 2 days a 5 % solution gave with TDI a soft instead of a brittle deposit and there was still an odour of isocyanate. After 7 days the odour had disappeared and the crystal cake was hard (table 3). Also ammonia solution and alcoholic solution was not investigated further because both contribute to undesired load of the waste water.

Good results were obtained with a water containing detergent. A concentration of o,1 % proved to be sufficient. 2 % detergent caused frothing and affords an unnessecary organic load of the drum contamination water. The detergent used was Lutensol AP 1o (a reaction product of nonylphenol with 1o mole ethylene oxide). This detergent is biological degradable. Trade names of comparati products are, as far as we know, Berol o9, NID 1ooo, Dowfax 9 N 1 Antarox CO-63o, Arkopal N 1oo, Lubrol N (?), Synperonic NP 1o, Sunapol NP 1oo, Ethylan KEO, Manro NP 9o, Triton N 1o1.

Decontamination with detergent solution, quantitative analysis

Further work was done with 5 l polyethylene buckets, from which the cristalline precipitate could be easier quantitative removed than from tin or glass vessels. 25 g TDI of 5o g MDI were spread on the inner walls of the bucket which was filled then with 4 l decontaminant. After 2 to 7 days at room temperature the liquid was filtrated and brought to investigation (s. table 2), the residue was collected and dried.

Table 2 Analytical values of decontamination solutions

Decontaminant	pH-value	N mg/l (Kjeldahl)	DOC mg/l organic carbon	sum of isocyanates and reaction products, colourimetry mg/l (calculated as TDA)	mg/l (calculated as MDA)	TLC chromatography Oligomers	Oth. Amines	BOD5 mg/l	Toxicity against bacteria (Sapromat)
water from TDI	7,o-7,8	4	1o	8,4		detectible	traces	<5	negative
water from crude MDI	7,1-7,5	<1	3		o,24 (uncertain)	traces	traces	<5	negative
water with o,1% Lutensol AP 1o from TDI	7,6	<1	not tested	4,o	----	not tested			

Analytical procedure

The pH-value was determined with pH-meter and Lyphan paper. Total nitrogen was determined by the Kjeldahl method. Soluted organic carbon (DOC) was determined by dry and by wet oxidation. Dry oxidation[1] was performed by MnO_2/CuO at 11oo °C, the generated CO_2 was titrated in organic solution with tributylmethyl ammonium hydroxide as total C. Carbonate C is determined after expelling CO_2 with $AgNO_3/HNO_3$ solution, the difference between total C and carbonate C gives organic C. The wet oxidation[2] was done with $K_2S_2O_8$ in presence of Ag^+/H_2SO_4.

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1) Method according to GIT, Fachzeitschrift für das Laboratorium, April 1975, S. 293-3o1

2) According to "Vom Wasser" Band 37, 197o S. 82-91, Verlag Chemi Weinheim

Primary amines were determined after diazotation and coupling reaction

a) qualitative by thin layer chromatography

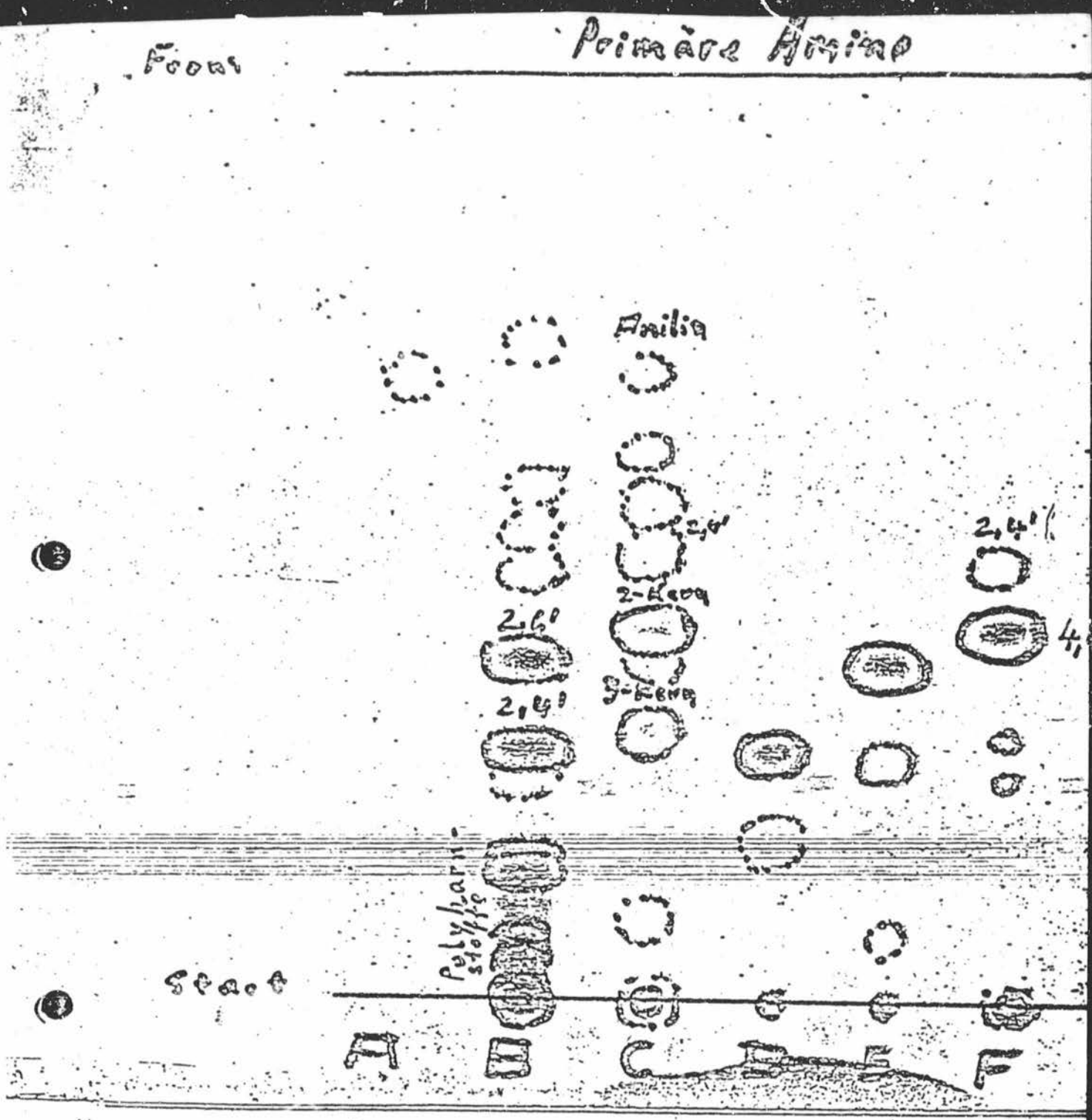
b) quantitative by photometry

For thin layer chromatography the reaction water was acidifid with 2nHCl, concentrated, made alkaline (2n KOH) and thrice extracted with 2oo ml ethyl ether. After evaporation the extract was solved in ethanol and chromatographed on silicagel 6oF254 (Merck). The solvent phase was toluene acetone 3:1. Development was performed twice. Diazotation with $NaNO_2$/HCL in the gasphase lasted 2o-3o seconds, then was sprayed with naphthylene diamine (o,4 % in ethanol). This process gives the sum of isocyanates and aromatic amines; a part or all of this amines could be generated during the analytic procedure, either by hydrolysis of in water dissolved isocyanate (not very probable) or by hydrolysis of dissolved oligomeric ureas. This analytic procedure is common for determination of isocyanates via the amines formed. How much of the amines is generated during analytical procedure or by analysis cannot be decided by this method. At the moment no certified method is published for the specific determination of isocyanates, their oligomers, aromatic amines and similar compounds in parallel, only the sum of aromatic amine compounds can be determined.

As can be seen from the attached chromatogram for comparison 2,4-TDA, 2,6-TDA and 4,4'-MDA as such (D, E and F) were used as standard and showed the same RF-Value as the extract of the decontamination water. The chromatogram of TDI decontamination shows besides 2,4- and 2,6-TDA also 4 stains, which may be related to oligomeric amines (ureas with terminated amino groups) and traces of 5 other compounds. The chromatogram of MDI-water showed 4,4'-MDA and 2,4'-MDA and 6-7 stainable traces of other compounds, included aniline.

The quantitative analysis of the decontamination water was performed by colourimetry of the azo dye from the acid extract, form according to the procedure of Meddle and Wood. As can be seen fro table 2, in water after TDI decontamination 8,4 mg/l TDI + react products (determined as TDA) were found, with water containing de gent only half of this amount. In water after decontamination of MDI only o,24 mg/l (calculated as MDA) were found; this is near the detection limit of the method and hence not precise.

The N-contents of the drinking water were found to be below 1 mg/ (usually o,3 - o,5 mg/l), dissolved carbon is in the range of 1 - 2 mg/l. These values are taken into consideration in the decontaminant values of table 2.



Kieselgel 60 F254 (Merck)

Toluol/Aceton 3:4

2x entwickelt

diazotiert

Naphthyl-
ethylendiamin

A Anilin
B TDI (T80)
C Roh-MDI (M20) } kg
D 2,4-TDA
E 2,6-TDA
F 4,4'-MDA

The biological oxygen demand[1] of this decontamination water is very low (BOD 5 below 5 mg/l, that means near the detection limit of this method) and the warburg test[2] shows no bacteria toxicity (see table 2). So this water should arise no problems if given undilated to waste water treatment.

Solid residue

The solid deposit was quantatively transferred from the Lupolen bucket to an earthenware disk and dried (in air and then in vacuum, over P_2O_5). 25 g TDI and 4ooo g water led to 22,7 g of dry deposit with a weak pink colour. 5o g raw MDI give 48,4 g of brown, brittle deposit (table 3). The weight of deposit was 6,8 % resp. 7,3 % higher than expected by theory; this is not fully understood.

Conclusion

We consider water as a suitable decontamination agent for isocyanate barrels, contact time should be not shorter than 7 days. The reaction water contains only a small amount of organic substances and biological degration should be no problem. Decontamination can be accelerated by the addition of o,1 % detergent like Lutensol AP 1o, but recommended time should still be at least 3 days. Reaction velocity with TDI is considerably lower than with MDI; after 7 days contact with drinking water there remains still an odour of TDI.

Encl.: table 3
chromatogram

1) Determined according to Deutsche Einheitsverfahren zur Wasser-, Abwasser-, Schlammuntersuchung (DEV), H5 b1), S. 15-19. Compara to OECD-method.

2) Determined according to DEV, L2, S. 1-3

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